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EVALUATION OF A CHEMICALLY PREPARED MAGNESIA AS A REFRACTORY RAW MATERIAL

by

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SUMMARY OF RESULTS

Samples of magnesium sulphite, as supplied by Spring Chemicals Limited were calcined in the temperature range 1000° to 1150°C (1832° to 2102°F) for periods of up to 3 hours. In an attempt to determine suitability for dead-burning, the magnesia samples so produced were compared for hydration stability with samples of calcined natural magnesite which were known to dead-burn to high densities. Selected samples were pelletized and dead-burned as calcined, after doping with silica or dicalcium ferrite, or after being ball-milled for 24 hours. The highest fired density of 3.28 g/cm^3 was achieved with a sample which had been calcined for 2 hours at 1150°C (2102°F) and doped with 2 percent by weight of dicalcium ferrite.

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INTRODUCTION

Magnesium compounds which consist essentially of sulphonates, are prepared as part of the chemical extraction of magnesia from dolomite ($(CaMg)CO_3$) according to a process developed by Spring Chemicals Limited, Masson, Quebec.

This company is interested in the possibilities of producing a dead-burned magnesia for use as a refractory raw material. The latter would be of a higher purity than dead-burned magnesite or sea-water magnesia.

To obtain dead-burned magnesia from these compounds, a two-stage process is involved. In the first stage, the material is heated in the temperature range 1000° to 1400°C (1832° to 2552°F), which causes decomposition to magnesia and sulphurous gases. In the second stage, the magnesia is compacted and dead-burned to a temperature of at least 1650°C (3002°F).

The object of this work was to determine the optimum conditions, in the first-stage calcination, which would produce magnesia suitable for subsequent compaction and dead-burning to yield a satisfactory refractory aggregate. The magnesium compound employed was the sulphite ($MgSO_3.6H_2O$) which contained some magnesium lignin material as impurity. The latter was present because the washing process, operated by Spring Chemicals Limited, was not taken to completion.

On an industrial scale, the sulphurous gases produced in the first-stage calcination would be scrubbed out to form acids.

Preliminary Work

Two samples of magnesia were initially submitted by Spring Chemicals for dead-burning trials. The calcination temperatures for these samples were given as 900° and 1370°C (1650° and 2500°F).

When water was added to the material which had been calcined at 900°C (1650°F), heat was evolved, indicating that this calcination temperature was too low. No further work was performed on this sample.

The material which had been calcined at 1370°C (2500°F) was pressed into discs having a cross sectional area of 6.45 cm^2 (1 $in.^2$) and being about 1.27 cm (1/2 in.) high under a pressure of

17.6 kg/cm^2 (25,000 psi). To facilitate pressing, 3 per cent water was added to the material. The discs were dried overnight at 80°C (176°F) and green densities were determined by weighing and measuring. The mean green density was 2.08 g/cm^3.

Firings were performed in a gas-fired furnace at 1650° and 1850°C (3002° and 3362°F) with no soaking period. Fired bulk densities of the discs were determined with a mercury balance and the mean values obtained were 3.16 g/cm^3 at 1650°C (3002°F) and 3.27 g/cm3 at 1850°C (3362°F).

These densities were deemed to be too low for refractory purposes and were probably due to either porosity in the magnesia particles or too large a crystal size, or both. The first-stage calcination temperature of 1370°C (2500°F) may have been too high and could account for both of these phenomena.

It was therefore decided to carry out a series of first-stage calcination trials to determine the optimum conditions for production of a material which would subsequently dead-burn to a high density.

Calcination Trials

Calcinations were performed on the raw material ($MgSO_3.6H_2O$) in an electric furnace for periods of 1, 2, and 3 hours at temperatures of 1000°, 1065°, and 1150°C (1832°, 1949°, and 2102°F).

To determine which of the calcined materials would be most likely to give a high bulk density on dead-burning, they were compared for hydration stability, in the loose form, with samples of natural magnesite which had been calcined under similar conditions and ball-milled for 6 hours. The latter samples were known to dead-burn to bulk densities in the range 3.30 to 3.40 g/cm^3(1) at 1650°C (3002°F) with no soaking period.

The hydration stability for loose magnesia powder would be expected to depend upon the specific surface i.e. the greater the specific surface the lower the hydration stability.

Hydration was carried out by steaming the samples for 1 hour in a household pressure cooker at 0.01 kg/cm^2 (15 lb/in.^{2}) pressure. Loss on ignition (hydration stability) was subsequently determined after heating, in an electric muffle furnace, for 2 hours at 1000°C (1832°F). The results are given in Table 1.

Note that of the calcined natural magnesites (Samples 10, 11, and 12) the most stable is Sample No. 12, with a value of 14.87 per cent for the hydration stability. Previous work(1) with these materials showed that this sample gave the highest bulk density on dead-burning, which indicates that specific surface alone cannot be used as a criterion for

predicting the fired density. Crystal size and size distribution must also be considered.

Dead-Burning Trials

Sample Nos. 4, 6, 8, and 9 were selected for dead-burning trials and discs of these materials were pressed as described earlier. After drying overnight at 80°C (176°F), the discs were fired in a gas-fired furnace at 1650°C (3002°F) with no soaking period and the fired densities determined with a mercury balance. The results are given in Table 1.

None of the selected samples fired to a bulk density within the range covered by the calcined natural magnesite, the highest being 3.27 g/cm^3 for the material calcined for 2 hours at 1150°C (2102°F). This value would probably be too low to make the dead-burned material a useful refractory aggregate.

A batch of Sample No. 4 (material calcined 1 hour at 1065°C (1949°F)) was doped with 5 percent by weight of Potter's Flint (SiO_2) and discs were pressed as described above. The discs were fired at 1650°C (3002°F) with no soaking period. The object of adding the silica was to form forsterite ($2MgO.SiO_2$) during the firing process, which would bond the material together thereby increasing the fired density. The fired density obtained on the mercury balance was 3.27 g/cm^3; an increase of 0.19 g/cm^3 over the pure magnesia. However, the discs were severely cracked probably due to the $\alpha \rightarrow \beta$ quartz change in the Potter's Flint during the rapid heat-up. Such a process would not be viable in a rotary kiln where the heat-up would also be very rapid.

Batches of Sample No. 8 (material calcined for 2 hours at 1150°C (2102°F)) were doped with calcium carbonate ($CaCO_3$) and ferric oxide (Fe_2O_3) in the correct ratio to give dicalcium ferrite ($2CaO.Fe_2O_3$) on firing to high temperature. The prepared batches contained the equivalent of 1, 2, and 5 percent by weight of dicalcium ferrite. This material acts as sintering aid and is used to accelerate dead-burning in the Alterra Process(2) for the production of dead-burned magnesia. The pressed discs were fired at 1650°C (3002°F) with no soaking period. The fired densities as determined with the mercury balance were as follows:

Wt % $2CaO.Fe_2O_3$	Fired Bulk Density (g/cm^3)
1	3.23
2	3.28
5	3.27

The values obtained show practically no change from that obtained with the pure magnesia (3.27 g/cm^3) fired under identical conditions.

TABLE 1

Hydration Stability of Calcined Raw Material in Loose Form

Sample No.	Calcination Temperature (°C)	Calcination Time (Hr)	Hydration Stability (% L.O.I.)	Fired Density (g/cm^3)
1	1000	1	15.27	-
2	"	2	15.11	-
3	"	3	14.03	-
4	1065	1	15.46	3.08
5	"	2	15.10	-
6	"	3	15.26	3.24
7	1150	1	14.36	-
8	"	2	17.74	3.27
9	"	3	21.21	3.15
10*	900	3	18.31	3.30
11*	1000	2	18.07	3.35
12*	1100	2	14.87	3.40

* Calcined natural magnesite, ball-milled for 6 hours(1).

In an attempt to eliminate any porosity from the magnesia crystals, a further batch of Sample No. 8 was ground in a ball-mill for 24 hours using high-alumina grinding media (balls). The charge: media ratio was 9:1. Discs were pressed as described above to a green density of 2.38 g/cm^3 and fired at 1650°C (3002°F) with no soaking period. The mean fired density was found to be 3.22 g/cm^3 which is somewhat lower than the value obtained for the same material in the unground condition (Table 1).

DISCUSSION

The results of this study have shown that the optimum calcination condition for the thermal decomposition of magnesium sulphite, as supplied by Spring Chemicals Limited, is a temperature of 1150°C (2102°F) maintained for a period of 2 hours. The magnesia obtained from this decomposition is difficult to dead-burn to a high density. The highest value obtained for the fired density at 1650°C (3002°F) with no soaking period was 3.28 g/cm^3; the raw material having been calcined for 2 hours at 1150°C (2102°F) and doped with 2 per cent by weight of dicalcium ferrite.

According to Spring Chemicals Limited(3) the product obtained from the calcination of the magnesium sulphite is 99.40% by weight magnesia. The principal impurity is iron oxide, (Fe_2O_3).

This suggests that the magnesia is of too high a purity to dead-burn in the same temperature range, i.e., 1650° to 1800°C (3002° to 3272°F) which is suitable for a natural magnesite. It is possible that the addition of dicalcium ferrite as a dead-burning aid is effective only in the presence of some other impurity, e.g., silica; this would explain the low densities obtained in this work when dicalcium ferrite was added.

The fact that the ball-milled material could be pressed to a green density of 2.38 g/cm^3, which is approximately the same value as was previously obtained with a natural magnesite(1), and yet only dead-burned to a density of 3.22 g/cm^3 suggests that the purity of the material may be too high for the dead-burning temperatures employed.

It is possible that the addition of tricalcium silicate may be more effective in promoting dead-burning to a high density, and further work should be performed along these lines.

It is claimed by Spring Chemicals Limited that the lime (CaO) content of the raw material can be controlled to within close tolerances in which case the amount of silica required to combine with a controlled lime impurity to form tricalcium silicate could be added prior to the initial calcination process. Such a raw material may be more suitable for refractory purposes than one which yields pure magnesia on calcination.

CONCLUSIONS AND RECOMMENDATIONS

The optimum calcination condition for the thermal decomposition of magnesium sulphite, as supplied by Spring Chemicals Limited, is a temperature of 1150°C (2102°F) maintained over a period of 2 hours.

The magnesia produced by the thermal decomposition of this raw material is probably of too high a purity to dead-burn satisfactorily in the temperature range 1650° to 1800°C (3002° to 3272°F) which would be suitable for a natural magnesite.

Additions of 5 percent by weight of silica (Potter's Flint) and up to 5 percent by weight of dicalcium ferrite are ineffective in increasing the fired density.

It is possible that additions of tricalcium silicate to the raw material may be effective in increasing the dead-burning rate. What would probably be more suitable would be the addition of silica to a raw material containing small quantities of lime (CaO) in order to form tricalcium silicate. Further work is recommended to investigate this possibility.

REFERENCES

1. Palfreyman, M., "Further Evaluation of a British Columbia Magnesite as a Refractory Raw Material", Dept. of Energy, Mines and Resources, Mines Branch Investigation Report IR 71-31, April, 1971.

2. Alterra, A.G., Brit. Pat. 394311, July 5, 1933.

3. Private Communication, Spring Chemicals Limited, Masson, Que., June, 1971.

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